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(54) FOAMING-TYPE RUST-PREVENTING MATERIALS

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SPECIFICATION

1. Title of the Invention

FOAMING-TYPE RUST-PREVENTING MATERIALS.

2. Scope of the Patent Claims

1. Foaming-type rust-preventing materials of the two-liquid, solvent-free group, characterized in that they contain the component A with a liquid epoxy resin and a liquid polycarboxylic acid anhydride as its necessary components, the component B with a liquid primary or secondary amine compound, a hardening promoting agent and a foaming agent as its necessary components and a non-reactive epoxy resin diluting agent with a molecular weight in the range of 300-4,000 and an electrically conductive powder as the necessary components other than the component A and/or the component B.

2. Foaming-type rust-preventing materials in accordance with claim 1, in which the rust-preventing materials are for use in automobiles.

3. Detailed Description of the Invention

The present invention pertains to foaming-type rust-preventing materials of the two-liquid, solvent-free group. More specifically, the present invention pertains to rust-preventing materials for use in automobiles, characterized in that they contain the component A with a liquid epoxy resin and a liquid polycarboxylic acid anhydride as its necessary components, the component B with a liquid primary or secondary amine compound, a hardening promoting agent and a foaming agent as its necessary components and a non-reactive epoxy resin diluting agent and an electrically conductive powder as the necessary components other than the component A and/or the component B.

In the past, in the joint part formed by spot welding of two pieces of flanges such as the rear fender arch part, the welded part of an engine room and a dashboard, etc., of an automobile, a gap may form at the seam of the flanges between the welded parts. Therefore, it is necessary to seal the gap. To achieve this object, a procedure involving the use of an automatic flow gun to extrude a spot sealer in the shape of beads for coating the joint part has been used in the past. However, with this procedure, it is difficult to coat the entire flange surface and thus water may seep in from the break in the sealer, causing rusting. To overcome this problem, a procedure involving the coating of the area around the flange joint part with a rust-preventing primer in a ribbon like shape has been carried out occasionally. This procedure, however, requires a solvent and thus there is a risk of fire at the time of spot welding. In addition, the procedure requires a drying process and thus it cannot be used during the conventional assembly process.

Therefore, we carried out extensive studies on various methods for ensuring the water tightness and corrosion resistance of the spot-welded parts and the area around it. We found that when the said parts were precoated with an excellent corrosion-resistant foaming material in a ribbon-like shape and were then welded, painted and baked, the water tightness could be ensured, the rust-preventing effect could be enhanced and the process could be made more efficient than the prior-art method. This method, however, is disadvantageous because the required performance characteristics for the rust-preventing sealant are very strict and thus the suitable materials that can be used are very limited.

The required performance characteristics for the rust-preventing sealant are as follows: In addition to the two performance characteristics, (1) the foaming property for improving the water tightness and (2) the rust-preventing property, they should also show (3) good workability for completing the ribbon-like coating process in a short period of time, (4) shower resistant property for withstanding the fat removing solution or zinc sulfate treatment, (5) electrical conductivity for ensuring that an area with insufficient coating will not form at the boundary between the sealant coated part and the uncoated part during the electrodeposition coating process, (6) the property that can ensure that the foaming and hardening will occur when the material is passed through the existing baking furnace (temperature 130-190°C) in the automobile manufacturing process, and (7) storage stability at normal temperature.

For example, the prior-art foaming sealant polyvinyl resin paste shows excellent performance characteristics when it is used only in the joint part of two panels. However, when it is used in the ribbon-like coating of a wide area including the smooth part outside of the joint part (e.g., a width of 10 cm) for the purpose of rust prevention, the coating will be washed away during the fat removing or zinc phosphate treatment process because of its poor shower resistant property. Furthermore, although a hot-melt-type material obtained by blending synthetic rubbers or waxes shows excellent coating workability, rust-preventing power, shower-resistant property, etc., when used without a solvent, it will become impractical when used as a foaming sealant because its coating working temperature and the decomposing temperature of the foaming agent are too close.

Therefore, we carried out extensive studies in order to develop rust-preventing materials with the various performance characteristics mentioned above and found that epoxy resin type rust-preventing materials with specific blending formula had excellent performance characteristics. This finding led us to develop the present invention.

In this way, the present invention can provide foaming-type rust-preventing materials of the two-liquid, solvent-free group that can be obtained by blending the component A with a liquid epoxy resin and a liquid polycarboxylic acid anhydride as its necessary components, the component B with a liquid primary or secondary amine compound, a hardening promoting agent and a foaming agent as its necessary components and a non-reactive epoxy resin diluting agent with a molecular weight in the range of 300-4,000 and an electrically conductive powder as the necessary components other than the said component A and/or the component B.

In the present invention, epoxy resins, acid anhydride type hardening agents, amine type hardening agents, hardening promoting agents for the acid anhydride type hardening agents, foaming agents, epoxy resin diluting agents and electrically conductive powders are used as the necessary components.

The epoxy resins used are polyepoxides that are liquid at room temperature and have more than two epoxy groups in each molecule. Preferred epoxy resins include, e.g., epoxy resins that can be obtained from bisphenol A or bisphenol F and epichlorohydrin, epoxy resins that can be obtained from hydrogenated bisphenol A and epichlorohydrin, etc. Other useful polyepoxides include, e.g., polyglycidyl ethers of novolak resins or polyphenol resins similar to the novolak resins, polyglycidyl ethers of such polyhydric alcohols as ethylene glycol, propylene glycol, diethylene glycol, glycerol, etc., glycidyl ethers of such carboxylic acids as phthalic acid, hydrogenated phthalic acid, etc., acryl copolymers having epoxy groups, epoxides of polybutadiene, etc. The viscosity of practical epoxy resins at room temperature should be less than 1,000 poises. Epoxy resins that are solid at room temperature are not desirable because it is difficult to obtain a blended material without the use of a solvent.

The polycarboxylic anhydride type hardening agents should be liquid at room temperature and are especially practical when their freezing point is below 0°C. It is not necessary that such hardening agents are made of one compound. For example, hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, tetrahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, methyl endomethylene tetrahydrophthalic anhydride, dodecenyl succinic anhydride, isomeric mixtures of these compounds, etc., may be used in the form of a properly blended mixture.

The primary or secondary amino compounds used should be liquid at room temperature. Any aliphatic amino compound, aromatic amino compound or their modified compounds may be used as long as they are used generally as a hardening agent of the epoxy resins. They include, e.g., ethylenediamine, diethylenetriamine, triethylenetetramine, menthenediamine, metaxylenediamine, 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane, bis(4-amino-3-methylcyclohexyl)methane, etc. In addition, compounds containing a primary or secondary amine group together with a tertiary amine group in the same molecule such as diethylaminopropylamine, *N*-aminoethylpiperazine, etc., may also be used. The aromatic amino compounds include, e.g., metaphenylenediamine, diaminodiphenyl methane, diaminodiphenyl sulfone, etc. The amino compounds obtained by modifying the said amino compounds for controlling the toxicity, the usable time, etc., include, e.g., epoxy resin adducts of the said amino compounds, adducts of such alkylene oxides as ethylene oxide, propylene oxide, etc., condensation products of an amino compound and a carboxylic acid known as cyanoethylated polyamines, ketone-masked polyamines and polyamide amines. Among these compounds, polyamide amines are used more practically from the standpoints of foul odor, toxicity, viscosity, shower-resistant property, etc.

As for the hardening promoting agents that can be used in the present invention, any compounds in the conventional epoxy resins of the polycarboxylic acid anhydride hardening type that are used as the hardening

promoting agent may be used. Concrete examples of such compounds are such tertiary amino compounds as dimethyl benzylamine, *N,N*-dimethylaniline, dimethylaminomethyl phenol, tris(dimethylaminomethyl) phenol, 2-ethyl-4-methyl imidazole, 1-benzyl-2-methyl imidazole, etc., such metal soaps as tin octenate, zinc naphthenate, etc., such metal alcoholates as sodium lithium alcoholate, etc., such metal complex salts as tin acetyl acetonates.

As for the foaming agent that can be used in the present invention, in principle, it can be of the organic type or inorganic type as long as it can be decomposed and generate a gas under the temperature conditions used during the process of hardening the epoxy resin by the acid anhydride hardening agent. In general, the use of foaming agents capable of undergoing decomposition in the temperature range of 130-190°C is practical. It is also practically important to use the foaming agent together with a foaming aid to adjust the decomposition temperature to be within the aforementioned range. Examples of such combinations include such nitroso compounds as *N,N'*-dinitropentamethylenetetramine, etc., and urea, azodicarbonamide and a metal salt, etc. As for the state of foaming, a very fine independent foaming state is desirable and from this standpoint, foaming agents of the organic type are better than those of the inorganic type.

The diluting agents that can be used in the present invention, in general, are the so-called non-reactive epoxy resin diluting agents containing no epoxy group in their molecules. They include, e.g., phenol modified aromatic polymers, phenol modified coumarone resins, formalin condensation products of xylene, oily substances formed during crude oil cracking, cyclopentadiene type resins obtained by copolymerization of vinyl monomers containing a hydroxyl group or an ester group, etc. It is necessary that these diluting agents are miscible with epoxy resins and are not reactive with the hardening agent and at the same time their number average molecular weight is in the range of 300-4,000. A diluting agent with a molecular weight less than 300 may reduce the mechanical strength of the hardening agent or may evaporate during the coating process, causing fire or labor hazards, and thus is not desirable. A diluting agent with a molecular weight greater than 4,000 is also not desirable because it may increase the viscosity of the composition, making the spray process difficult.

In addition to the components mentioned above, the rust-preventing materials of the present invention should contain an electrically conductive powder, the main purpose of which is to ensure tight adhesion of the electrodeposition paint to the edge of the coated rust-preventing material. Concrete examples of such electrically conductive powders are, in addition to electrically conductive carbon black and graphite, such metal powders as zinc, copper, silver, aluminum, etc. However, the use of such metal powders may result in an oxidation-induced decrease in the electrical conductivity and loss of stability of the blended material. Therefore, electrically conductive carbon black and graphite without the aforementioned shortcomings are more practically used.

In the present invention, if necessary, blending agents other than the necessary components mentioned above may be added. Such blending agents include, e.g., adhesion improving agents for the oil surface formed when cold rolled steel plate is coated with the rust-preventing oil, extending agents, fillers, pigments, flame resistant agents, etc. Concrete examples of such blending agents include silicone type surface active agents, bitumen, glass fibers, quartz powders, calcium carbonate, talc, mica, colloidal silica, asphalt, etc.

In the present invention, the components mentioned above are divided into two liquid components, one containing the epoxy resin and the other containing the amino compound. It is necessary that these two components are prepared in such a way that their viscosity at 25°C is in the range of 1-1,000 poises or preferably 10-500 poises so that they can be used for coating at room temperature. The epoxy resin containing component (A) should contain the epoxy resin and the polycarboxylic acid anhydride as the necessary components and may contain desired amounts of the epoxy resin diluting agent and the electrically conductive powders. The amino compound containing component (B) should contain the primary or secondary amino compound, the hardening promoting agent and the foaming agent as the necessary components and may also contain desired amounts of the epoxy resin diluting agent and the electrically conductive powders.

The quantitative ratio of the epoxy resin and the polycarboxylic acid anhydride in the (A) component can be selected properly. However, it is usually so selected that 0.2-1.5 or preferably 0.3-1.2 acid anhydride groups are present for each epoxy group. When the amount of the polycarboxylic acid anhydride used is decreased, the effect of the concomitant use of the amine type hardening agent will decrease. In contrast, when the amount of the polycarboxylic acid anhydride used is increased, the storage stability may be reduced or an excess amount of the unreacted polycarboxylic acid anhydride will remain, decreasing the rust-preventing power.

The mixing ratio of the primary or secondary amino compound and the hardening promoting agent in the (B) component may also be selected properly. In general, however, the amount of the primary or secondary amino compound used is such that 0.1-2.5 or preferably 0.3-2.0 amino acid active hydrogen atoms would be present for each epoxy group and the amount of the hardening promoting agent used is such that 0.05-30 weight parts or preferably 0.2-20 weight parts of the hardening agent would be present for every 100 weight parts of the epoxy resin used when the (A) component and the (B) component are mixed. When the number of the amino group active hydrogen atoms is decreased, the shower resistant property would decrease and the corrosion resistance would also decrease. In contrast, when the number of the active hydrogen atoms is increased, the shortcoming unique to the amine type hardening agent such as foul smell and toxicity would no longer be negligible and in addition the adhesiveness and rust-preventing power would also tend to decrease. When the amount of the hardening promoting agent used is reduced, hardening would become insufficient, lowering the adhesion force and rust-preventing power. In contrast, if the amount of the hardening promoting agent used is increased, the flexibility of the hardened material would decrease.

The blended amount of the foaming agent or the mixture of the foaming agent and the foaming aid (called the foaming agent component below) in the component (B) is controlled by the amount of the gas generated by the foaming component used. If the volume of the rust-preventing material hardened without added foaming agent component is set to be 100, it is desirable that the blended amount is so adjusted that the foaming magnification would be in the range of 110-300% or preferably 120-250% in order to ensure the air tightness and rust-preventing property. Concretely, it is appropriate to set the foaming agent component to make up 0.3-20 wt. % or preferably 0.5-10 wt. % of the component (B).

There is no specific restriction as to the quantitative compositions of component (A) and component (B) of the rust-preventing material of the present invention as long as the various conditions mentioned above can be satisfied. However, it is necessary that the mixture of component (A) and component (B) contains 10-130 weight parts or preferably 15-100 weight parts of the epoxy resin diluting agent and 0.5-20 weight parts or preferably 1-15 weight parts of the electrically conductive powder for every 100 weight parts of the combined amount of the epoxy resin and the hardening agent. When the amount of the diluting agent used is too small, the flexibility of the hardened material will not be sufficient. In contrast, use of an excessive amount is not desirable because poor hardening may occur or the hardness of the hardened material may be reduced. When the amount of the electrically conductive powder blended is too small, the electrodeposition paint will not adhere to the flange of the hardened material during the electrodeposition coating process, reducing the rust-preventing power. In contrast, when the amount blended is too small, the viscosity of the system will increase, making the spray process difficult.

In general, the mixing ratio of component (A) and component (B) used in the present invention should be such that the number of the acid anhydride groups is in the range of 0.2-1.5 and the number of the amino group active hydrogen atoms is in the range of 0.1-2.5 for every one epoxy group. In addition, the ranges used should be such that the total number of the acid anhydride groups and the amino active hydrogen atoms is greater than 1.0. As long as the blending ratios mentioned above are maintained, the rust-preventing agent of the present invention can have the advantage that the ratio of the main agent and the hardening agent may be varied in a wide range. The component (A) and the component (B) may be premixed and the mixture is used for coating or the solutions of these two components may be coated individually and then mixed on the coated material. The hardened products obtained by either of these two procedures will yield the same performance characteristics.

For painting, a brush-like material may be used for coating the mixture of the two components by hand, or a bead gun or an air spray device designed in such a way that the two solutions can be mixed at the front end of the device may be used for coating.

The rust-preventing materials of the present invention obtained as described above show excellent workability and also excellent safety because they are essentially of the solvent-free type. Furthermore, they show excellent performance characteristics in terms of air tightness, shower resistant property, flexibility and adhesiveness and they are quite acceptable in terms of foul smell or toxicity. Therefore, these materials are very appropriate as the rust-preventing materials of the part joining the automobile panels.

The present invention will be explained in more detail with the use of actual examples given below. In these actual examples, the parts and % used are expressed in standard weight unless specified otherwise.

Actual Example 1

Glycidyl ether type epoxy resin of bisphenol A (epoxy equivalent 180, viscosity 13,000 cP/25°C, Epicoat 828, a product of Shell Kagaku Co.), an isomerized product of the equal amount mixture of 4-methyl tetrahydrophthalic anhydride and 3-methyl tetrahydrophthalic anhydride (freezing point below -20°C), polyamide amine (amine value 385, viscosity 350 cP/75°C, Parsamide 140, a product of Daiichi General), tin octenate, non-reactive epoxy resin diluting agent (phenol modified aromatic polymer, viscosity 200 cP/25°C, number average molecular weight 370, Sintaron 702, a product of Tokyo Jushi Kogyo Co.), carbon black (HB-600, a product of Asahi Carbon Co.), a foaming agent component of a 2:1 mixture of azodicarbonamide (Uniform AZ, a product of Otuska Kagaku) and zinc stearate (decomposition temperature 170°C), talc and silicone oil (SH-28 PA, a product of Tore Silicon Co.) were blended according to the blending recipes given in Table 1 and a heat hardening two-solution material consisting of solution A and solution B was prepared. In this process, a three-roll was used to disperse the blended material.

The viscosity at 25°C of solution A and solution B thus obtained was measured with the use of a B type viscometer. Two air spray devices (compression ratio of 1:50 for both devices) with the weight ratio of solution A to solution B of 1:1 was used to extrude the solutions in a ribbon-like form through the mouth of an internal mixing type one-head gun equipped with a flat nozzle in front of its head for coating a soft steel plate with adhered rust-preventing oil.

Immediately after coating, a separate soft steel plate was subjected to two-spot welding to obtain an experimental panel. This panel was allowed to stand at normal temperature for 3 hours and then sprayed with 60°C warm water at a pressure of 3 kg/cm² in a fog-like form for studying the shower resistant property of the coated part. This panel was then immersed in an anionic electrodeposition paint solution and an electric current was passed through under a voltage of 200 V at 25°C for 2 minutes. The panel was washed with water and then allowed to undergo hardening by baking at 160°C for 30 minutes. Various performance characteristics were then determined. The results obtained are given in Table 1.

Table 1

Experiment No.	Comparison Example				Example of the present invention
	1	2	3	4	5
<u>Solution A</u>					
Epoxy resin	100	100	100	100	100
Methyl tetrahydrophthalic anhydride	-	50	50	50	50
Carbon black	2	-	2	2	2
Silicone oil	0.2	0.2	0.2	0.2	0.2
<u>Solution B</u>					
Polyamide amine	50	50	50	50	50
Tin octanoate	3	3	3	3	3
Liquid non-reactive type diluting agent	50	50	-	50	50
Talc	50	50	50	50	50
Carbon black	2	-	2	2	2
Foaming agent component,	5	5	5	-	5
<u>Performance characteristics</u>					
External appearance (shower resistance, protruding out) ^{note 1)}	Washed away by shower	Good	Protruding out frequently	Good	Good
Air tightness ^{note 2)}	Good	Good	Good	Poor	Good
Corrosion resistant property ^{note 3)}	Rusted	Rusted	Good	Good	Good

Note 1) Examined whether the sealant was washed away by shower or protruded out from the bent part between the welding points.

Note 2) Filled with water to examine whether the bent part between the welding points had been sealed by foaming.

Note 3) The welded panel was placed in a 5% salt water spraying room (35°C) for 700 hours to examine the rusting condition around the sealant.

The results described above indicate that the rust-preventing materials of the present invention exhibit excellent performance characteristics in terms of shower resistant property, air tightness and rust-preventing property. However, the air tightness became poor when the foaming agent component was not used and the shower resistant property and the rust-preventing power deteriorated when methyl tetrahydrophthalic anhydride was not used, i.e., the satisfactory performance characteristics could not be expected when any of the components constituting the present invention was absent.

Next, comparison examples were used to further explain the performance characteristics of the rust-preventing materials of the present invention.

Comparison Example 1

One hundred parts of polyvinyl chloride for use in a paste (Zeon 121, a product of Nippon Zeon), 100 parts of dioctyl phthalate, 100 parts of calcium carbonate, 3 parts of barium type stabilizer and 5 parts of the foaming agent component made of a 2:1 mixture of azodicarbonamide (Uniform AZ) and zinc stearate (decomposition temperature 170°C) were thoroughly mixed. The mixture thus obtained was used to coat a soft steel plate using a 1-mm doctor blade. The experimental procedure identical to that used in Actual Example 1 was then carried out. It was found that the majority of the product was washed away by shower. When the remaining part was allowed to harden and foam, the air tightness was found to be poor and rusting occurred at the boundary part between the sealant part and the electrodeposition coat film.

Comparison Example 2

In experimental number 5 of Actual Example 1, the composition with the foaming agent blended at the solution A side was prepared. An experimental procedure exactly identical to that used in Actual Example 1 was carried out. It was found that the viscosity of solution A increased markedly during the storage and smooth coating could not be achieved.

Actual Example 2

An experimental procedure exactly the same as that used in Actual Example 1 was carried out except that toluene sulfonyl hydrazide derivative (Unihol NH #1000, a product of Suiwa Kasei Kogyo, decomposition temperature 140°C) was used as the foaming agent component. The product thus obtained showed excellent external appearance, air tightness and corrosion resistant property.

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